

PATENT SPECIFICATION

NO DRAWINGS

991387



991387

Date of Application and filing Complete Specification May 28, 1963.

No. 21313/63.

Application made in United States of America (No. 202659) on June 15, 1962.

Complete Specification Published May 5, 1965.

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Index at acceptance: —C2 C(2A1, 2A2, 2A6, 2R18, 2R20)

Int. Cl.:—C 07 c

COMPLETE SPECIFICATION

Process for Recovering Polyamines from Polyisocyanate Reaction Products

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and 5 by the following statement:—

THIS INVENTION relates to a process for recovering polyamines from polyisocyanate reaction products by hydrolysis.

The term "polyisocyanate reaction products" as used in the specification is meant to include only those products which can be formed by a reaction involving the isocyanate group (—NCO). The term includes compounds which can be derived from isocyanates, whether or not the actual manner in which the compound is obtained involved the use of other reactants. For example, it includes the polyurea of toluene diisocyanate whether it be made from toluene diisocyanate and water or from phosgene and excess tolylenediamine. Likewise, it includes urethanes whether they are made by reaction of isocyanates with alcohols or by the reaction of chloroformates with amines. 20 It does not include compounds made from isocyanates by reactions which do not involve the —NCO group, such for example as ring halogenated aromatic diisocyanates made by halogenation of aromatic diisocyanates.

In practice the hydrolysis process of the present invention will normally be applied to polyisocyanate reaction products which are in the form of residues or remnants, for example residues resulting from the preparation of polyisocyanates by the phosgenation of polyamines, which preparation is accompanied by the formation of tarry materials.

Remnants occur, for instance, in the production of polyurethanes, especially in such final forms as foams, fibres, and moulded articles. These scrap materials and tarry residues contain some of the relatively expensive polyamine starting materials used in the initial formation of the polyisocyanate reaction product.

Hydrolysis is recognized as a means of recovering polyamines from polyisocyanate reaction products, such as phosgenation tars, and scrap polyurethane plastics and elastomers, including cellular polyurethane products. Most of these materials are quite resistant to hydrolysis, and aqueous solutions of strong acids or base have been required to effect hydrolysis at ordinary pressures and temperatures. The cost of reagents and the complications involved in separating the hydrolysis products from the reaction medium make hydrolysis processes using acidic or basic agents unattractive.

In an effort to avoid these problems, superatmospheric pressure hydrolysis processes have been developed. These processes involve treating the polyisocyanate reaction products with water in the liquid state at temperatures of about 160—250° C. and pressures ranging from 10 to 40 atmospheres. While they avoid the problems associated with acidic or basic hydrolysis, they require the use of costly high pressure equipment which restricts their usefulness.

According to the present invention polyamines are recovered from polyisocyanate reaction products (as defined above) by a hydrolysis process in which a non-volatile polyisocyanate reaction product is hydrolyzed with steam superheated to a temperature of 200—400° C.

By the process of the invention, polyamines can be obtained from phosgenation tars, urethane polymers, polyisocyanate dimers and

[Price 4s. 6d.]

- trimers, and a wide variety of reaction products which can be made from polyisocyanates and active hydrogen compounds.
- The process is restricted in that the material being subjected to hydrolysis must be essentially non-volatile under the conditions employed and must not form intermediate hydrolysis products, short of the amine, which are volatile under the conditions employed. The term "non-volatile" as used herein means substantially non-volatile at the temperature of the steam employed. These restrictions are necessary because polyisocyanate reaction products or intermediate hydrolysis products which are volatile under the conditions employed will be prematurely carried away from the hydrolysis zone by the passage of the superheated steam.
- Since the steam is superheated the hydrolysis is effected in the absence of condensed water.
- The process can be conducted at atmospheric pressure or at a slightly elevated pressure. This permits the use of equipment of usual construction, rather than the high pressure equipment which is required by hydrolysis processes employing superheated water in the liquid state.
- The isocyanate reaction products which can be hydrolyzed by the process of the invention can be derived from aliphatic, cycloaliphatic, arylalkyl and aromatic polyisocyanates, as long as the requirements for non-volatility are met. Representative examples of isocyanates which may form such reaction products are:
- Aliphatic Diisocyanates
- Tetramethylene diisocyanate
 - Hexamethylene diisocyanate
 - Cycloaliphatic Diisocyanates
 - Methylcyclohexane-2,4-diisocyanate
 - 4,4'-Diisocyanatodicyclohexylmethane - Arylalkyl Diisocyanates
 - m-Kylylene diisocyanate - Aromatic Diisocyanates
 - Toluene-2,4-diisocyanate
 - Toluene-2,6-diisocyanate
 - 1,3-Phenylene diisocyanate
 - Cumene-2,4-diisocyanate
 - 4,4'-Diisocyanatodiphenyl methane
 - 4,4'-Diisocyanatodiphenyl ether
 - 1,5-Naphthalene diisocyanate
 - 4,4'-Diisocyanatodiphenyl
 - 3,3'-Dimethyl-4,4'-diisocyanato-diphenyl methane
 - 5-Chlorotoluene-2,4-diisocyanate
 - 4-Chlorophenylene-1,3-diisocyanate
 - 3,5-Dichlorotoluene-2,4-diisocyanate - Aromatic Triisocyanates
 - Toluene-2,4,6-triisocyanate
 - 4,4',4"-Triisocyanatotriphenyl methane
 - 2,4,4'-Triisocyanatodiphenyl ether
- The process finds its greatest use in the recovery of diamines from the reaction pro-

ducts of diisocyanates, because diisocyanates are commercially more important than triisocyanates. The non-volatility requirements are in general met by isocyanate reaction products prepared from either diisocyanates or triisocyanates. In general, the isocyanate reaction products derived from monoisocyanates are too volatile to be hydrolyzed effectively by the new process. The recovery of diamines from reaction products of the toluene diisocyanate, 4,4'-diisocyanatodiphenylmethane, hexamethylene diisocyanate, and 4,4'-diisocyanatodicyclohexylmethane represents the most important application of the process, owing to the present commercial importance of these diisocyanates. Obviously, new developments in the isocyanate field may change this situation.

Isocyanate reaction products may be divided conveniently into two major classes; namely, products formed by the reaction of the isocyanato group with active hydrogen compounds (i.e. compounds giving a positive Zerewitiusoff test), and products formed by addition or condensation polymerization reactions of the isocyanato group.

Representative examples of the first class of products include ureas, which can be prepared by reacting isocyanates with ammonia, primary amines and secondary amines, or by reacting many isocyanates with water; urethanes, which can be prepared from isocyanates and alcohols or phenols; amides, prepared by reacting aliphatic or aromatic carboxylic acids with isocyanates, accompanied by the loss of carbon dioxide; biurets, from isocyanates and ureas; and allophanates, from isocyanates and urethanes. This list is not exclusive, but it does include the most important examples of this class. The compounds in this class may be characterised by the presence of the



This class of reaction products includes most of the materials which are likely to be subjected to hydrolysis by the present process on a commercial scale. It includes phosgenation rags, which consist mainly of ureas or polymeric ureas, though possibly also of smaller amounts of biuret, trimer, and carbodiimide, polyurethane plastics, elastomers and foams; and polyurea and polyamide fibres and plastics.

The second class of reaction products that can be hydrolyzed by the process of the invention includes the isocyanate dimers, isocyanate trimers (isocyanurates) and carbodiimides. These compounds are made from isocyanates by reactions involving polymerization of the isocyanato group. Examples of such compounds are well-known in the aromatic series and though aliphatic isocyanate dimers have never been reported in

- the literature, aliphatic isocyanate trimers and carbodiimides are known. While the process of the invention may find little commercial application to the isocyanate reaction products of this class at present, it is nevertheless capable of hydrolyzing even the isocyanate trimers which are known for their great stability toward hydrolysis and other reactions. The isocyanate dimers and trimers contain the structural unit —N—C— where R
- $$\begin{array}{c} \text{R} \\ | \\ \text{O} \end{array}$$
- represents the radical to which the isocyanate group was originally attached. Carbodiimides have the structure R—N=C=N—R where R has the same meaning.
- As previously stated the essence of the invention lies in the use as hydrolysing agent of superheated steam at temperatures in the range 200—400° C. Superheated steam may be described as water vapour above its equilibrium condensation point. It does not contain any liquid water, nor can it exist in the presence of a separate liquid water phase. Water vapour can be at equilibrium with liquid water at temperatures ranging from 200—374.2° C. if pressures ranging from about 15—218 atmospheres are employed. While hydrolysis can be carried out at such high pressures, it is one aim of this invention to avoid the need for expensive heavily-constructed processing equipment. Thus, it is preferred to operate the present process at pressures of 1—5 atmospheres. It is surprising that liquid water is not required to bring about hydrolysis under these conditions.
- In practising the process of this invention, it is usually desirable to employ a considerable excess of steam over that required by theory to effect hydrolysis. When a large excess of steam is employed, the hydrolysis reaction will usually proceed more rapidly presumably as a result of good physical contact of the steam with the material being hydrolyzed. Furthermore, it is often desirable to strip away the polyamine almost as rapidly as it is formed, in order to prevent excessive exposure of the polyamine to the relatively severe temperature conditions which exist in the hydrolysis zone. Many of the polyamines which can be obtained by this process do not steam distil readily, and a large quantity of steam is required for their removal.
- It has been found practical to use 2—10 kg. of superheated steam/kg. of polyamine to be produced. Smaller quantities of steam can be used, but the rate of hydrolysis may be reduced. Greater quantities of steam are generally not required except in the case of very high boiling polyamines, and then only when it is desirable to remove the polyamine from the hydrolysis zone by steam stripping. In the case of the by-product tars or residues resulting from the phosgenation of *m*-tolylenediamines, 5—8 kg. of steam/kg. of recovered diamine is preferred.
- Difficulty in meeting these requirements has been encountered with reaction products derived from monoisocyanates. For example, if N,N'-diphenylurea is treated with superheated steam at 300° C., it will be found that most of the urea distills with the steam unchanged. It is true that a trace of aniline is formed before all of the diphenylurea has been distilled away, but the process is not practical for recovering aniline from this material. By reducing the amount of steam used, a greater amount of the diphenylurea can be hydrolyzed before it is carried away by the superheated steam, but other difficulties, such as ensuring proper contact of the steam with the diphenylurea, again limit the usefulness of the process as a means for hydrolyzing diphenylurea. Even the non-volatile urethane prepared by reacting two moles of phenyl isocyanate with one mole of polytetramethylene ether glycol of molecular weight about 1000 cannot be effectively hydrolyzed to aniline, because this urethane when exposed to superheated steam at temperatures of about 300° C. is changed back to the free glycol and N,N'-diphenylurea, the latter being removed from the system by steam-distillation almost as rapidly as it is formed by hydrolysis of the original urethane. As with diphenylurea, a small trace of aniline is again formed, but the urea leaves the hydrolysis zone before any appreciable quantity of aniline has been produced. These difficulties have only been experienced with mono-isocyanates. The isocyanate reaction products derived from polyisocyanates (including diisocyanates) are sufficiently non-volatile for hydrolysis to be easily completed before any substantial quantity of the polyisocyanate reaction product has distilled from the hydrolysis zone with the superheated steam.
- While the hydrolysis of most polyisocyanate reaction products will start at 200° C., the rate of the hydrolysis reaction can be increased significantly by operating at higher temperatures, e.g. 250—350° C. By operation at these temperatures hydrolysis can be substantially completed in contact times ranging from 2 to 8 hours. While hydrolysis proceeds at temperatures down to 200° C. or even lower, the times required to produce practical results will be quite extended. With materials that are particularly difficult to hydrolyze, such as the aromatic diisocyanate trimers, temperatures approaching the upper limit of 400° C. may be desirable. Hydrolysis will also occur at temperatures above 400° C., but thermal decomposition reactions which produce by-

- product tars may reduce the quantity of polyamine obtained.
- With most polyisocyanate reaction products, the progress of the hydrolysis may be followed by measuring the rate at which carbon dioxide is evolved. This is relatively easy to estimate, because the vapours leaving the hydrolysis zone consist largely of steam, polyamine and carbon dioxide, from which the steam and polyamine may be readily condensed, the volume of the residual carbon dioxide gas being measured with a wet test meter. In the case of those isocyanate reaction products which do not evolve carbon dioxide during hydrolysis, such as amides, the progress of the reaction may be followed by determining the quantity of amine in a sample of condensed vapours or in a sample of the mass taken from the hydrolysis zone.
- Determination of the amine present in these samples may be accomplished in a variety of ways including titration with sodium nitrite, gas chromatography, infrared or ultraviolet spectrography, and polarography.
- The hydrolysis may be carried out in a variety of ways. In the case of infusible polyisocyanate reaction products in the particulate form of powder or small granules, the superheated steam may be passed through the particles in a column. If the rate of steam flow is properly adjusted, infusible powders or small granules can be fluidized, with the resulting well known excellent contact between the gas and solid. In employing an arrangement of this type, it is usually desirable to remove the product polyamine about as rapidly as it is formed, since otherwise there is danger that it will wet the infusible powder and cause sticking or caking and so interfere with further hydrolysis.
- When employing this procedure, it is desirable to heat the isocyanate reaction product to a temperature over 100° C. before introducing the steam, to prevent wetting the particles with steam condensate which might cause caking. The necessary heat may be furnished by introducing a hot inert gas stream, or by heaters surrounding the column.
- Liquid polyisocyanate reaction products may be hydrolyzed in an agitated vessel, by introducing the steam underneath the surface of the liquid.
- While the above procedures are of use in specialized cases, there is a preferred procedure which has more general applicability. This comprises suspending the isocyanate reaction product in an inert high-boiling liquid and passing the superheated steam through the suspension. This can be done in a variety of conventional types of equipment, including columns, towers, pipe line reactors and agitated vessels.
- The process may be operated both batch-wise and continuously, but is conveniently performed batch-wise in agitated vessels which may be heated either entirely by means of the superheated steam, or with the aid of auxiliary heating means. The passage of superheated steam may be started at any temperature, but it is preferable first to heat the suspending medium and isocyanate reaction product to about 100° C. or above to prevent the condensation of water in the reaction medium and to reduce the amount of steam required.
- While any liquid which is essentially non-volatile and inert may be used to suspend the isocyanate reaction products, the naphthenic hydrocarbon oils recommended as a medium for the process of U.S. Patent 2,889,257 are especially preferred. These refined oils, of the nature of a lubricating oil bright stock, consist essentially of carbocyclic ring structures having paraffinic side chains. The majority of the carbocyclic rings are saturated, but a small proportion usually less than 10% may be aromatic. These refined oils are quite non-volatile and have good thermal stability under the conditions employed. They are poor solvents for polyisocyanate reaction products, which however can readily be dispersed in them, especially in the presence of suitable surface active agents which will be described later.
- This process involving a suspension of the isocyanate reaction product in naphthenic oil is very convenient for recovering *m*-tolylenediamines from the by-product tars or solid residues resulting from their phosgenation, especially from the solid residues which are produced by the process of U.S. Patent 2,889,257. Since the solid residues produced by the process are already suspended in the naphthenic hydrocarbon oils described above, treatment with steam may be carried out either directly or after increasing the concentration of solid phosgenation residue in the oil by partial filtration or thickening.
- Surface active agents which are particularly useful in suspending polyisocyanate reaction products in the naphthenic hydrocarbon oils are described in U.S. Patent 2,810,681. They are normally used in lubricating or fuel oils to reduce sludge formation and to disperse any solids which form or are already present. In the present process these surfactants appear to act in a similar manner by dispersing and preventing the agglomeration of the polyisocyanate reaction product during the hydrolysis. These surfactants are preferably addition type copolymers containing in combined form as their essential monomeric components, (a) copolymerizable ethylenically unsaturated compounds which contain only one polymerizable ethylenic linkage, at least one of which components is amine-free and contains from 8 to 18 carbon atoms in an aliphatic hydrocarbon

chain, which in the polymer is not part of the main chain, and (b) a compound containing a basic amino-nitrogen in the side chain, the said copolymer containing 0.1% to 3.0% by weight of basic amino-nitrogen.

The amine-free components employed in the preparation of these copolymers include the long chain alkyl methacrylates such as lauryl methacrylate, tridecyl methacrylate, octadecyl methacrylate, n-octyl methacrylate, 2-hexylmethacrylate, s-capryl methacrylate, n-decyl acrylate, and such compounds as vinyl laurate, ar-dodecyl-styrene, lauryl-ethyl maleate, lauryl fumarate, dodecyl-hexyl-styrene. Suitable compounds are more particularly described in U.S. Patents 2,666,044, 2,737,495 and 2,737,452.

The second component of the copolymer, which contains the basic nitrogen in the side chain, may be exemplified by such compounds as β -diethylaminoethyl methacrylate, p -diethylaminoethyl-styrene, 2-methyl-5-vinyl-pyridine, 4-vinyl-pyridine, 4-dimethylamino-cyclohexyl methacrylate, β -dicyclohexyl-aminoethyl methacrylate, diallylamine; other basic amino-nitrogen compound including primary, secondary and tertiary amines, as more particularly exemplified in the patents above mentioned may be used. As illustrated in these patents, the basic amino-nitrogen containing component that imparts sludge-inhibiting and dispersing properties can be introduced through the use of appropriate copolymerizable monomers containing primary, secondary, and tertiary amino-nitrogen that is attached ultimately to the chain of the polymer as part of an extra-linear substituent group in which the nitrogen is joined extranuclearly only to non-benzenoid carbon atoms. The amino groups can be attached to the main copolymer carbon chain through strictly hydrocarbon structures or through ether, ester, or amide linkages. The amount of first and second component employed will of course be that required to give in the final polymer a basic nitrogen content of 0.1% to 3.0% of the total weight of the polymer. Usually 75% to 95% of the long chain methacrylate with 5% to 25% of the basic nitrogen-containing monomer will give a desired product.

These surfactants may also contain additional copolymerizable components which may be added to the polymer to maintain the basic nitrogen content within the range specified above, as more particularly illustrated in U.S. Patents 2,666,044 and 2,737,496.

The preferred surfactant is a 90:10 (by weight) copolymer of technical lauryl methacrylate and β -diethylaminoethyl methacrylate, but any of the surfactants disclosed above may be used to advantage. The surfactant should be used in amounts equal to 0.1—3.0% based on the weight of naphthenic

hydrocarbon oil. The addition of 0.3—0.5% of surfactant to naphthenic oil has been found to be adequate to maintain phosphogenation residues well dispersed throughout the course of the hydrolysis reaction.

In recovering amines from polyurethanes derived from isocyanates and high molecular weight polyalkyleneether polyols, hydrolysis may be conveniently carried out by suspending the polyisocyanate reaction product in a portion of the polyalkyleneether polyol contained in the polyurethane rather than the naphthenic oil described above. If sufficient steam is used to remove the polyamide, the polyalkyleneether glycol portion of the polyurethane will remain in the hydrolysis zone along with the polyol which was present at the start of the hydrolysis. A portion of the polyalkyleneether polyol in the hydrolysis vessel can be drawn off and a new charge of polyurethane material added and the passage of steam repeated to produce additional polyamine and polyalkyleneether polyol. Since most polyalkyleneether polyols are temperature stable and resistant to hydrolysis, temperatures in the range 300—350° C. may be employed. In such a process surfactants are not required.

In the case of polyureas, polyurethanes and polyamides which are derived at least partially from low molecular weight glycols, polyols, amines, and carboxylic acids, polyamines produced by the process of the invention will be accompanied by these low molecular weight intermediates. For example, if a polyurethane prepared from hexamethylene diisocyanate and 1,4-butanediol is subjected to steam hydrolysis, both hexamethylenediamine and butanediol will be stripped from the hydrolysis zone and when condensed will be present as a mixture. In most cases, this is not a serious disadvantage, since the materials usually can be separated easily by fractional distillation, and it may be of advantage economically since both of the materials recovered may be of value. Naturally, if the reaction products hydrolyzed are prepared by reactions involving more than one polyisocyanate, a mixture of polyamines will be recovered. It should be pointed out that polyurethanes derived from polyisocyanates and polyester glycols are capable of undergoing hydrolysis of the polyester linkages in the polymer as well as of the linkages derived by reaction of the isocyanato groups, and the value of the process of this invention in recovering polyamines from polyurethanes containing polyester portions depends to a certain extent on the materials from which the polyester glycol or polyol was derived originally.

When the process of the invention is operated with sufficient superheated steam to remove polyamine about as rapidly as it is formed, the polyamine may be isolated by

- condensing water and polyamine vapours leaving the hydrolysis zone, and distilling to separate water and polyamine from any non-volatile materials which may have been entrained during the passage of steam. Partial condensation of the vapours from the hydrolysis zone may often be used to advantage if the polyamine is sufficiently high boiling and has little tendency to steam distil. When the quantity of steam employed to effect hydrolysis is not sufficient to remove the polyamine from the hydrolysis zone, the polyamine can be isolated by conventional means such as distillation or extraction.
- Certain polyisocyanate reaction products which may be subjected to hydrolysis by the process of the present invention may contain free polyisocyanates. This is particularly true of such materials as phosgenation residues, since removal of the last traces of polyisocyanate may be very difficult. If superheated steam is passed directly through a polyisocyanate reaction product containing a free polyisocyanate, a portion of the polyisocyanate will often steam distil away from the hydrolysis zone unchanged and be converted to a polyurea at some point in the equipment beyond the hydrolysis zone. Since polymeric ureas are quite high melting and non-volatile they may form throughout the equipment beyond the hydrolysis zone solids which may eventually plug the equipment or interfere with the operation of the process. This can be avoided if polyisocyanate reaction products containing some free polyisocyanate are first contacted with water at a temperature near 100° C. to convert the polyisocyanate to the less volatile polyureas before the hydrolysis. Alternatively another active hydrogen-containing material such as ammonia, an alcohol, an amine or hydrogen sulphide, may be used to react with the free polyisocyanate before the hydrolysis.
- The following Examples illustrate the invention. Parts and proportions are by weight unless otherwise indicated.

EXAMPLE 1

Powdered toluene diisocyanate phosgenation residue obtained from the process of United States Patent 2,810,681 is washed well with petroleum ether to remove the naphthenic hydrocarbon oil used in producing it. The washed phosgenation residue is air-dried to remove most of the petroleum ether, and placed in an oven at 70° C. to complete the removal of solvent. The dry phosgenation residue is placed in a column which is equipped for heating and has provision for the introduction of steam at the bottom. The column is connected at its upper end to a downward water-cooled condenser, so that steam and condensable vapors passing up the column may be collected by condensation. The column and the phosgenation residue contained in it are heated to above 100° C. Sufficient steam superheated to a temperature of about 200° C., is introduced to fluidize the bed of dry phosgenation residue. When the steam is first introduced, the temperature of the vapors above the fluidized bed of phosgenation residue is 101° C., but owing to the heat content of the superheated steam, (plus the heat introduced by the column heaters) the temperature rises to about 240° C. in about 1/2 hr. Once the temperature has reached 240° C., the passage of superheated steam is continued for about 4 hours, during which time the temperature of the vapour over the fluidized bed ranges between about 240 and 245° C. The velocity of the steam in the column is about 6 cm./sec. The vapors leaving the column, which comprise water, *m*-tolylenediamine and carbon dioxide, are passed through the water-cooled condenser. 200 parts of condensate is obtained for every 100 parts of residue initially charged to the column. The condensate is analyzed for *m*-tolylenediamine by polarographic analysis, standardized with pure *m*-tolylenediamine. The solution is found to contain a quantity of amine equivalent to about 7 parts of *m*-tolylenediamine for each 100 parts of the phosgenation residue initially charged.

EXAMPLE 2

About 400 parts of a naphthenic hydrocarbon oil having a Saybolt Universal viscosity of 150 seconds at 99° C. is placed in a heated vessel equipped with an agitator, a condenser leading to a receiver, and an inlet placed near its bottom for the introduction of super-heated steam. About 150 parts of dry powdered phosgenation residue prepared as described in Example 1 is introduced into the oil. The resulting slurry is agitated, and heat is supplied to the vessel. When the temperature of the slurry reaches 190° C., the flow of superheated steam through the slurry is started. The temperature of the super-heated steam ranges from 350° to 370° C. The passage of steam is continued for a period of two hours at a rate of about 200 parts/hr., during which time the temperature of the slurry increases from 190° to 250° C. All condensable vapors are collected by means of the condenser. Substantially all of the carbon dioxide evolved as a result of hydrolysis passes through the condensation system to the atmosphere. A total of about 407 parts of distillate is collected, and analysis of this condensate by polarographic assay shows the presence of 31.9 parts of *m*-tolylenediamine. This is equivalent to 21.2 parts of *m*-tolylenediamine per 100 parts of phosgenation residue.

- Following the passage of steam, the reaction vessel is opened and examined. It is found to contain some small lumps of material above the surface of the oil. The lumps have the appearance of an expanded or gas-blown plastic mass.
- EXAMPLE 3**
- The process of Example 2, is repeated except that 8 parts of 90:10 copolymer of technical lauryl methacrylate and β -diethylaminoethyl methacrylate is added to the 400 parts of naphthenic hydrocarbon oil prior to the passage of steam. Polarographic analysis of the condensate produced in this run shows that 31.7 parts of *m*-tolylenediamine is produced per 100 parts of dry phosgenation residue.
- The reaction vessel is again opened for inspection. The walls of the vessel are free of material above the oil level, and no lumps of the type found following the run in Example 2 are present. The non-hydrolyzable solids remaining in the oil are dispersed uniformly.
- EXAMPLE 4**
- About 2020 parts of the naphthenic hydrocarbon oil used in Example 2 is placed in a heated vessel equipped with an agitator, condenser, and steam inlet. About 15 parts of a 90:10 copolymer of technical lauryl methacrylate and β -diethylaminoethyl methacrylate is added to the oil. Agitation is started in the vessel, and 960 parts of a tarry distillation residue, resulting from the preparation of a 4:1 mixture of toluene-2,4- and toluene-2,6-diisocyanate by phosgenation of mixed *m*-tolylenediamine isomers, is added at room temperature. The distillation residue contains 32.4% toluene diisocyanate and 67.6% non-volatile phosgenation by-products.
- The slurry of distillation residue is first treated with water to convert free toluene diisocyanate into polymeric ureas. To do this the contents of the vessel are heated to 100° C. and 3 parts of triethylenediamine is added. About 350 parts of a 2% solution of hydrogen peroxide in water is then added over a period of about 1 hour. The triethylenediamine and hydrogen peroxide are added to catalyze the reaction of water with the toluene diisocyanate. The mixture is refluxed for about 2 hours, after which time the evolution of carbon dioxide ceases, indicating completion of the reaction between water and toluene diisocyanate. The water remaining in the vessel is then distilled off, and the temperature of the dry oil slurry is raised to about 260° C., at which point superheated steam at a temperature of about 315° C. is introduced. The passage of superheated steam at a rate of about 300 parts per hour is continued for 8 hours, during which the temperature of the oil
- in the hydrolysis vessel ranges from 310 to 335° C. The condensate obtained consists of two layers; an aqueous layer containing *m*-tolylenediamine and a small layer of steam distilled naphthenic hydrocarbon oil. The oil layer is separated from the aqueous phase and may be returned to the hydrolysis vessel for re-use.
- Water is then removed from the aqueous layer by distillation at atmospheric pressure. The *m*-tolylenediamine remaining after the removal of water, is distilled under vacuum at about 10 mm. Hg. About 419 parts of distilled *m*-tolylenediamine is recovered, and the substantially non-volatile residue remaining after distillation of the diamine amounts to 19 parts. If it is assumed that the toluene diisocyanate initially present in the tar is converted in theoretical amount to *m*-tolylenediamine, the yield of *m*-tolylenediamine from the phosgenation residue portion of the initial tar sample amounts to 35.5 parts of diamine/100 parts of phosgenation residue.
- EXAMPLE 5**
- About 1508 parts of naphthenic hydrocarbon oil as used in Example 2, and 15 parts of a 90:10 copolymer of technical lauryl methacrylate and β -diethylaminoethyl methacrylate are placed in an agitated vessel as described in Example 2. About 500 parts of crude 4,4'-diisocyanatodiphenylmethane is added to the oil with agitation at about 30° C. The crude 4,4'-diisocyanatodiphenylmethane is about 85% pure, the remainder being phosgenation tars. The temperature of this mass is raised to 100° C. and 2 parts of triethylenediamine is added, followed by about 260 parts of water. The 4,4'-diisocyanatodiphenylmethane is reacted with the water by refluxing at a temperature of 100—110° C. for one hour. The excess water over that required to convert the diisocyanate to polymeric ureas is removed by distillation at atmospheric pressure, and the temperature of the oil in the vessel is raised to about 260° C. Superheated steam at about 315° C. is introduced at a rate of 250 parts/hr for 4 hours while the temperature of the oil is maintained at 320—360° C. 4,4'-Methylenedianiline is recovered from the condensate by distillation. The 4,4'-methylenedianiline distills at about 220—235° C. at 1 mm. Hg. About 111 parts of the diamine is obtained. The diamine has a freezing point of 84.7° C. and gives the same infrared absorption spectrum as a known sample of 4,4'-methyleneedianiline.
- EXAMPLE 6**
- A solid polymeric urea is prepared by reacting 920 parts of toluene diisocyanate (having a composition corresponding to 80 parts of toluene-2,4-diisocyanate and 20 parts

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toluene-2,6-diisocyanate) with about 200 parts of water in the presence of 1467 parts of naphthenic hydrocarbon oil as specified in Example 2 and two parts of triethylendiamine. The reaction of the diisocyanate with water is conducted at about 100° C. under reflux. When the toluene diisocyanate has been completely converted to polymeric ureas as indicated by a cessation of the evolution of the carbon dioxide, excess water is removed by distillation at atmospheric pressure. The slurry of polymeric ureas in oil is placed in a reaction vessel as described in Example 2. The slurry is heated to about 200° C. and the passage of superheated steam at about 315° C. is initiated. Hydrolysis is continued at temperatures ranging from 300 to 340° C. for 12 hours with a steam flow of about 250 parts/hr. The condensate 70

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consists of an aqueous layer containing *m*-tolylenediamine and an oil layer. The oil layer is separated and saved for re-use. Water is removed from the aqueous layer by distillation at atmospheric pressure, and the crude *m*-tolylenediamine remaining is recovered by distillation under vacuum. A total of 563 parts of distilled diamine is recovered, which corresponds to 87.3% of the theoretical amount obtainable based on the starting toluene diisocyanate used for the preparation of the polymeric ureas.

EXAMPLE 7

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A polymeric urea is prepared from hexamethylene diisocyanate by reacting 352 parts of hexamethylene diisocyanate dissolved in 1892 parts of ethyl acetate with an excess of 109 parts of water in the presence of 5 parts of triethylendiamine and 30 parts of 3% hydrogen peroxide in water. The reaction is carried out by adding the water to the solution of hexamethylene diisocyanate in an agitated vessel equipped with a reflux condenser. The water is added over about 1 hour at 77° C., at the end of which time the reaction is complete, no further carbon dioxide coming off. The resulting slurry of polymeric ureas in ethyl acetate is agitated for 16 hours, filtered and washed with petroleum ether. The solid cake is dried in the air.

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The polymeric urea so produced is charged into about 1500 parts of naphthenic hydrocarbon oil, described in Example 2, containing 20 parts of a 90:10 copolymer of technical lauryl methacrylate and β -diethylaminooethyl methacrylate. The slurry of polymeric ureas in oil is heated to a temperature of about 200° C., and the flow of superheated steam through the slurry is initiated. Over about 1 hour the temperature is raised from 200 to 300° C. Passage of superheated steam at about 315° C. is continued for an additional 2 hours at a rate of 200 parts/hr., the temperature in the hydrolysis zone ranging from 300 to 350° C.

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Water is removed from the condensate by distillation at atmospheric pressure. The residue remaining after the atmospheric distillation is distilled under vacuum. About 183 parts of distilled hexamethylene diamine is obtained in this fashion. This corresponds to a theoretical yield of 75.5% based on the hexamethylene diisocyanate initially used. The infrared absorption spectrum of the recovered hexamethylene diamine is identical with that of an authentic sample of hexamethylene diamine.

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EXAMPLE 8

250 parts of toluene-2,4-diisocyanate, dissolved in 1200 parts of dry σ -dichlorobenzene, is trimerized by the addition of 25 parts of diethylamine and 5 parts of ρ -dimethylaminomethylphenol. The solution is stirred for about 30 minutes at room temperature, after which solids appear and the reaction mass becomes almost solid. A small portion of the solids is washed with petroleum ether, dried in a vacuum oven at 100° C., and examined by infrared analysis. The solids exhibit strong absorption at 5.85 Angstrom units, which is recognized as the trimer absorption wave length.

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The slurry of trimer in σ -dichlorobenzene is transferred to a hydrolysis vessel as described in Example 2 containing 1500 parts of naphthenic hydrocarbon oil and 20 parts of a 90:10 copolymer of technical lauryl methacrylate and β -diethylaminooethyl methacrylate. First the σ -dichlorobenzene is removed by distillation at atmospheric pressure. When the temperature of the oil containing the trimer reaches about 200° C., flow of superheated steam at about 315° C. through the slurry is initiated. The flow of steam is continued at a rate of about 250 parts/hr. while maintaining the temperature of the oil slurry at about 330–365° C. for about 4 hours. The condensate obtained consists of two layers, a large aqueous layer containing *m*-tolylenediamine and a small layer of steam-distilled naphthenic hydrocarbon oil. The naphthenic hydrocarbon oil layer is separated and the aqueous layer is distilled. About 174 parts of distilled *m*-tolylenediamine is obtained. This corresponds to a yield of 81.5% of theory.

WHAT WE CLAIM IS:—

1. A process for obtaining a polyamine which comprises hydrolyzing a non-volatile polyisocyanate reaction product (as hereinbefore defined) with superheated steam at a temperature of 200–400° C.
2. Process according to claim 1, wherein the polyisocyanate reaction product is contained in a phosgenation tar, or polyurethane, polyurea or polyamide.
3. Process according to claim 1 or 2, wherein the polyamine produced is removed

- from the hydrolysis zone by distillation with excess of the superheated steam.
4. Process according to any one of the preceding claims, wherein the polyisocyanate reaction product is heated to at least 100° C. before hydrolyzing it with the superheated steam.
5. Process according to any one of the preceding claims, wherein the polyisocyanate reaction product initially contains some unreacted polyisocyanate from which it is freed before it is contacted with the superheated steam.
6. Process according to any one of the preceding claims, wherein the polyisocyanate reaction product is a phosgenation tar produced in the phosgenation of *m*-tolylenediamine, 4,4'-diaminodiphenylmethane, hexamethylene diamine, or 4,4'-diaminodicyclohexylmethane.
7. Process according to any one of the preceding claims, wherein the polyisocyanate reaction product is treated with the superheated steam while dispersed in an inert organic liquid.
8. Process according to claim 7, wherein the dispersion is heated to at least 100° C. before hydrolyzing it with the superheated steam.
9. Process according to claim 7 or 8, wherein the inert organic liquid is a naphthenic hydrocarbon oil.
10. Process according to any one of claims 7-9, wherein the inert organic liquid contains a surfactant.
11. Process according to claim 9, wherein the naphthenic hydrocarbon oil contains as a surfactant a copolymer obtained from 90 parts by weight of technical lauryl methacrylate and 10 parts by weight of β -diethylaminoethyl methacrylate.
12. Process according to any one of claims 1-6 wherein a polyurethane derived from a polyalkylene ether glycol or polyol is hydrolyzed in suspension in a polyalkylene ether glycol or polyol identical with that from which it is derived.
13. Process for obtaining a polyamine according to claim 1, substantially as hereinbefore described.
14. Polyamines obtained by a process claimed in any one of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agent,
14, South Square,
Gray's Inn,
London, W.C.I.